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(57) Abstract

A laminate and a protective garment resistant to the permeation of chemicals have a fabric base sheet and continuous impervious layers supported by the base sheet and comprising layers of fluoropolymer and butyl rubber. According to the invention, the laminate and the protective garment also include a continuous polyamide layer.

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LAMINATE AND PROTECTIVE CLOTHING FABRICATED THEREFROM

The present invention relates to a laminate and protective clothing fabricated therefrom, which are intended to be used as protective means against poisonous/aggressive chemicals, e.g. in connection with hazardous chemical emergencies, decontamination work etc.

Protective clothing or garment made of such a laminate must be flexible and highly resistant, not only to the chemicals concerned but also to mechanical damage. To this end, laminates and clothing made of a fabric base sheet coated with different types of protective layers have been suggested. Such known highly resistant protective clothing and laminate comprise a fabric base sheet coated with a layer of fluoropolymer and butyl rubber. Clothing of this type provides good resistance to permeation of aggressive substances, such as acetone, acetonitrile, ammonia, carbon disulfide, chlorine, dimethylformamide, ethyl acetate, hexane, methanol, nitrobenzene, sodium hydroxide, sulfuric acid, tetrachloroethylene and toluene. The demands for resistance and protective capacity have however been raised, and it is now required that the material should also possess high resistance to permeation of dichloromethane, diethylamine and tetrahydrofuran. Prior art protective clothing is not resistant to these substances.

One object of the present invention therefore is to improve the clothing or garment mentioned above and give it high resistance to the permeation of such substances. According to the invention, this object is achieved by fabricating the laminate and the protective clothing or garment as stated in claims 1 and 6, respectively.

The invention thus resides in supplementing the lami-

advantageous to use a copolymer of caprolactam and hexamethylenediamine and caprolactam.

The use of a continuous polyamide layer in laminates for protective clothing is however previously known from EP-A-0,360,208. The laminate according to this publication is however built up differently and comprises a base sheet of nonwoven polypropylene on both sides laminated to a multilayer film sheet which, counting from the base sheet, consists of a layer of polyamide, a layer of polyethylene vinyl alcohol, a layer of polyamide and a surface layer of low-density polyethylene.

The use of a continuous polyamide layer is also disclosed in US-A-4,833,010 describing a multilayer chemical barrier fabric consisting of a base sheet of nonwoven polypropylene laminated on both sides to a multilayer film sheet material. The multilayer material on one side of the base sheet comprises, counting from the base sheet, a layer of polyethylene vinyl alcohol, a layer of polyamide and a heat-sealable surface layer of polyethylene. The multilayer material on the other side of the base sheet comprises, counting from the base sheet, a layer of polyethylene vinyl acetate, a layer of polyamide and a heat-sealable surface layer of polyethylene. Thus, also the laminate according to this publication is built up differently as compared with the laminate of the present invention.

The laminate according to the invention is manufactured by coating a fabric, consisting e.g. of polyamide fibres and serving as base sheet, with the different materials which are to form the different layers of the laminate, optionally after using an adhesive to increase the bonding strength between the different layers and the base sheet. Materials other than polyamide fibres can be used for the base sheet, e.g. aramide fibres (such as KEVLAR® Nomex® from E. I. Du Pont de Nemours and Company, USA), polyamide fibres (such as KERMEL® from Rhône-Poulenc S.A., France).

In one embodiment of the invention, one side of the base sheet can be coated with fluoropolymer and the other with butyl rubber, whereupon the layer of polyamide is applied to the free surface of the layer of butyl rubber. A more preferred embodiment of the laminate and the protective clothing however utilises a layer of butyl rubber also between the base sheet and the layer of fluoropolymer since the base sheet will thus be more efficiently protected against aggressive chemicals. One alternative way of applying the continuous polyamide layer is using a finished or preproduced polyamide film which is placed on the base sheet and the other layers of the laminate just before this is to be introduced in a Rotocure machine. This type of lamination yields a laminate having the properties aimed at.

The fabric base sheet may be e.g. a woven fabric having a weight per unit area or grammage of 85 g/m^2. In one of the preferred embodiments of the laminate and the protective clothing, respectively, one side of the base sheet can be coated, e.g. by spreading, with a layer of butyl rubber. A suitable coating weight per unit area may be 175 g/m^2. To the layer of butyl rubber may then be applied a layer of fluoropolymer, e.g. in a coating weight of 200 g/m^2. On the other side of the base sheet, the layer of butyl rubber may have a coating weight of e.g. 150 g/m^2. The polyamide layer, which is applied to this layer of butyl rubber, either by coating or as a finished or preproduced polyamide film, may have a weight per unit area of e.g. 70 or 100 g/m^2. A laminate manufactured in this way has very high flexibility and very high chemical resistance and resistance to permeation of chemicals, also of the above-mentioned chemicals dichloromethane, diethylamine and tetrahydrofuran.

A polyamide fabric was pretreated with an adhesion-promoting agent based on butyl rubber and isocyanate, and was coated on each side with a layer of butyl rubber. The layer of butyl rubber consisted of a pasty coating mixture which, in addition to uncured butyl rubber, contained curing agent, filler, antioxidants, plasticiser and lubricant (stearic acid). A coating was thereafter applied to the layer of butyl rubber by spreading a pasty coating mixture containing fluoropolymer, curing agent, filler, plasticiser and lubricant.

On the other side of the polyamide, a polyamide layer was applied on the layer of butyl rubber. The polyamide layer was applied by spreading a pasty mixture of polyamide and a solvent and, optionally, also a plasticer. To form the different pasty mixtures, petrol was used as liquid medium for the butyl rubber pastes, alcohol/water (90:10 mixture) as solvent for the polyamide paste and methyl ethyl ketone as solvent for the fluorocarbon rubber. Instead of applying the polyamide layer by spreading, it can be applied as a finished or preproduced film which is applied to the base sheet coated with the other materials, just before this is to be introduced into the vulcaniser or curing apparatus, as previously pointed out.

Between each spreading operation, the material was dried, and after the final coating and drying operations the material was cured at about 150°C. The resulting product had very high flexibility, pliability and chemical permeation resistance as well as sufficient resistance to all the substances mentioned above, whereby to satisfy the altered requirements for chemical protective clothing against hazardous chemicals according to US standard NFPA 1991 (1990 Edition).

EXAMPLE 1

was provided with a bonding layer on both sides by spreading a bonding agent solution thereon. First, a solution was prepared by mixing the following ingredients:

chlorinated butyl rubber (1.2% by weight of chlorine)	100 parts by weight
magnesium oxide	0.15 parts by weight
zinc oxide	10 parts by weight
stearic acid	1 part by weight
pyrogenic silicic acid (AEROSIL® 300)	25 parts by weight
colour pigment	3 parts by weight
titanium dioxide	5 parts by weight

These ingredients were dissolved in a mixture of technical grade petrol (4 parts by volume) and toluene (1 part by volume) to a dry solids content of about 50% by weight. To obtain the bonding agent solution, about 10% by weight of isocyanate (e.g. DESMODUR® RF) was added to the solution thus prepared. The isocyanate-containing mixture was used to form the bonding agent coatings on both sides of the fabric. After drying, one side of the fabric was coated by spreading a similar solution of the same composition, however without the admixture of isocyanate. This spreading yielded a layer of butyl rubber on one side of the fabric. After drying, a layer of fluoropolymer was applied on the layer of butyl rubber. The layer of fluoropolymer consisted of a 50% by weight solution in technical grade petrol/toluene (4:1) having the following ingredients:

fluorocarbon rubber (VITON® B50)	100 parts by weight
barium sulfate	20 parts by weight
titanium dioxide	15 parts by weight
magnesium oxide	15 parts by weight
colour pigment	5 parts by weight
N,N'-dicinnamyliden-1,6-hexamethylene diamine (DIAK® 3)	3.5 parts by weight

After drying, the opposite side of the fabric was coated by spreading a similar solution of the same composition, however without the admixture of isocyanate. After drying, a polyamide layer was finally applied by spreading thereon a mixture of 20 parts by

weight of polyamide (ULTRAMID® 6A) in 80 parts by weight of a mixture of 10% by volume water and 90% by volume ethanol. After drying of this final layer, the laminate was cured at about 150°C for 20 min.

When testing the finished laminate, it was found that it complied with the regulations currently proposed as new standard in 1991 by the National Fire Protection Association, USA (NFPA Standard on Vapor-Protective Suits for Hazardous Chemical Emergencies, 1990 Edition) and listing resistance to permeation of acetone, acetonitrile, ammonia, carbon disulfide, chlorine, dimethylformamide, ethyl acetate, hexane, methanol, nitrobenzene, sodium hydroxide, sulfuric acid, tetrachloroethylene, toluene, dichloromethane, diethylamine and tetrahydrofuran.

EXAMPLE 2

Example 1 was repeated, but the polyamide layer was here applied as a finished or preproduced polyamide film (nylon 6) having a thickness of 50 µm (obtained from ATOCHEM S.A. in France). This film was applied to the uncured butyl rubber layer on the side of the base sheet opposite to the layer of fluorocarbon rubber, just before the forthcoming laminate was to be introduced in a Rotocure machine. In this machine, curing was carried out at 150°C at a belt speed of about 30 m/h, giving a curing time of about 10 min.

As appears from the test results reported below, this laminate also fulfilled the regulations according to the proposed new standard of 1991 by the National Fire Protection Association, USA (NFPA Standard on Vapor-Protective Suits for Hazardous Chemical Emergencies, 1990 Edition). The test result with dichloromethane when testing the clothing material as such did however not give a result fully complying with the proposed NFPA standard, probably

[illegible] samples. The tests were conducted according to said proposed new standard, both with the original material (un-

treated), with material subjected to flexural fatigue testing [NFPA 1991, Section 5-5.1(a)], and with material subjected to abrasion resistance testing [NFA 1991 Section 5-4.1(a), (b), (c) and (d)]. The tests were carried out by an independent testing institute (TRI/Environmental, Inc., Austin, Texas, USA). The permeation resistance tests were carried out according to ASTM F739-85, testing temperature 27°C, testing time 3 h and chemical concentration 99.5% with continuous contact.

TABLE 1

Untreated original material

Chemical	Time to permeation breakthrough min.			Permeation rate $mg/cm^2 \cdot h$			Minimum detectable rate $\mu g/cm^2 \cdot min$
	cell No.			cell No.			
	1	2	3	1	2	3	
acetone	ND	ND	ND	NA	NA	NA	0.14
acetonitrile	ND	ND	ND	NA	NA	NA	0.14
ammonia	ND	ND	ND	NA	NA	NA	0.14
carbon disulfide	ND	ND	ND	NA	NA	NA	0.14
chlorine	ND	ND	ND	NA	NA	NA	0.14
dichloromethane	144	116	ND	NA	0.78	5.4	0.14
diethylamine	ND	ND	ND	NA	NA	NA	0.14
dimethylformamide	ND	ND	ND	NA	NA	NA	0.14
ethyl acetate	ND	ND	ND	NA	NA	NA	0.14
n-hexane	ND	ND	ND	NA	NA	NA	0.14
methanol	ND	ND	ND	NA	NA	NA	0.14
nitrobenzene	ND	ND	ND	NA	NA	NA	0.14
sodium hydroxide	ND	ND	ND	NA	NA	NA	0.14
sulfuric acid	ND	ND	ND	NA	NA	NA	0.14
tetrachloroethylene	ND	ND	ND	NA	NA	NA	0.14
tetrahydrofuran	ND	ND	ND	NA	NA	NA	0.14
toluene	ND	ND	ND	NA	NA	NA	0.14

ND = not detected NA = not applicable

TABLE 2

Flexed material

Chemical	Time to permeation breakthrough min.			Permeation rate $mg/cm^2 \cdot h$			Minimum detectable rate
	cell No.			cell No.			
	1	2	3	1	2	3	$\mu g/cm^2 \cdot min$
acetone	ND	ND	ND	NA	NA	NA	0.14
acetonitrile	ND	ND	ND	NA	NA	NA	0.14
ammonia	ND	ND	ND	NA	NA	NA	0.14
carbon disulfide	ND	ND	ND	NA	NA	NA	0.14
chlorine	ND	ND	ND	NA	NA	NA	0.14
dichloromethane	ND	ND	ND	NA	NA	NA	0.14
diethylamine	ND	ND	ND	NA	NA	NA	0.14
dimethylformamide	ND	ND	ND	NA	NA	NA	0.14
ethyl acetate	ND	ND	ND	NA	NA	NA	0.14
n-hexane	ND	ND	ND	NA	NA	NA	0.14
methanol	ND	ND	ND	NA	NA	NA	0.14
nitrobenzene	ND	ND	ND	NA	NA	NA	0.14
sodium hydroxide	ND	ND	ND	NA	NA	NA	0.14
sulfuric acid	ND	ND	ND	NA	NA	NA	0.14
tetrachloroethylene	ND	ND	ND	NA	NA	NA	0.14
tetrahydrofuran	ND	ND	ND	NA	NA	NA	0.14
toluene	ND	ND	ND	NA	NA	NA	0.14

ND = not detected NA = not applicable

TABLE 3

Abraded material

Chemical	Time to permeation breakthrough min.			Permeation rate $mg/cm^2 \cdot h$			Minimum detectable rate $\mu g/cm^2 \cdot min$
	cell No.			cell No.			
	1	2	3	1	2	3	
acetone	ND	ND	ND	NA	NA	NA	0.14
acetonitrile	ND	ND	ND	NA	NA	NA	0.14
ammonia	ND	ND	ND	NA	NA	NA	0.14
carbon disulfide	ND	ND	ND	NA	NA	NA	0.14
chlorine	ND	ND	ND	NA	NA	NA	0.14
dichloromethane	ND	ND	ND	NA	NA	NA	0.14
diethylamine	ND	ND	ND	NA	NA	NA	0.14
dimethylformamide	ND	ND	ND	NA	NA	NA	0.14
ethyl acetate	ND	ND	ND	NA	NA	NA	0.14
n-hexane	ND	ND	ND	NA	NA	NA	0.14
methanol	ND	ND	ND	NA	NA	NA	0.14
nitrobenzene	ND	ND	ND	NA	NA	NA	0.14
sodium hydroxide	ND	ND	ND	NA	NA	NA	0.14
sulfuric acid	ND	ND	ND	NA	NA	NA	0.14
tetrachloroethylene	ND	ND	ND	NA	NA	NA	0.14
tetrahydrofuran	ND	ND	ND	NA	NA	NA	0.14
toluene	ND	ND	ND	NA	NA	NA	0.14

ND = not detected NA = not applicable

CLAIMS

1. Laminate resistant to the permeation of chemicals, consisting of a fabric base sheet and continuous impervious layers supported by said base sheet and comprising layers of fluoropolymer and butyl rubber, c h a r a c t e r i s e d in that the continuous impervious layers of the laminate also comprise a polyamide layer.

2. Laminate as claimed in claim 1, c h a r a c t e r i s e d in that the layers of fluoropolymer and polyamide are applied to opposite sides of the base sheet.

3. Laminate as claimed in claim 1 or 2, c h a r a c t e r i s e d in that the polyamide layer is separated from the base sheet by a layer of butyl rubber.

4. Laminate as claimed in claim 1, 2 or 3, c h a r a c t e r i s e d in that the layer of fluoropolymer is separated from the base sheet by a layer of butyl rubber.

5. Laminate as claimed in any one of claims 1-4, c h a r a c t e r i s e d in that the polyamide layer is based on a copolymer of adipic acid/hexamethylenediamine and caprolactam.

6. Protective clothing resistant to the permeation of chemicals, consisting of a laminate having a fabric base sheet and continuous impervious layers supported by said base sheet and comprising layers of fluoropolymer and butyl rubber, c h a r a c t e r i s e d in that the continuous impervious layers of the laminate also comprise a polyamide layer.

7. Protective clothing as claimed in claim 6, c h a r a c t e r i s e d in that the layers of fluoro-

8. Protective clothing as claimed in claim 6 or 7, c h a r a c t e r i s e d in that the polyamide layer is separated from the base sheet by a layer of butyl rubber.

9. Protective clothing as claimed in claim 6, 7 or 8, c h a r a c t e r i s e d in that the layer of fluoropolymer is separated from the base sheet by a layer of butyl rubber.

10. Protective clothing as claimed in any one of claims 6-9, c h a r a c t e r i s e d in that the polyamide layer is based on a copolymer of adipic acid/hexamethylenediamine and caproclactam.

INTERNATIONAL SEARCH REPORT

International Application No PCT/SE 90/00551

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC5: B32B 27/12, D06M 17/08, A62D 5/00, A62B 17/00, A41D 31/02

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
IPC5	B32B; D06M; A62D; A62B; A41D

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in Fields Searched[8]

SE,DK,FI,NO classes as above

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category *	Citation of Document,[11] with indication, where appropriate, of the relevant passages[12]	Relevant to Claim No.[13]
A	US, A, 4792480 (P. X. FREUND ET AL.) 20 December 1988, see claims 1-3,6-8 --	1,6
A	US, A, 4355065 (R. P. DEMOTT) 19 October 1982, see claims 1,3,5 --	1,6
A	DE, A1, 3502300 (DEUTSCHE SEMPERIT GMBH) 16 January 1986, see claims 1,4,5 --	1,6
A	EP, A1, 0320258 (PALL CORPORATION) 14 June 1989, see claims 1,6,9 --	1,6

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* Special categories of cited documents: [10]

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Date of the Actual Completion of the International Search

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ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO. PCT/SE 90/00551

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the Swedish Patent Office EDP file on 90-11-01
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Patent document cited in search report	Publication date	Patent family member(s)		Publication date
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		GB-A-	2209706	89-05-24
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